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STATISTICAL THEORY OF THE CRITICAL POINT

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ABSTRACT 32269

A statistical theory of the critical point is presented in this work. The theory is applied to an examination of phase changes in other systems.

The existing phenomenological theory of the critical point (Ref. 1), /54* which is based on the equation given by van der Waals, is not satisfactory, because it does not enable one to employ the method of Gibbs in examining both the thermodynamics of a system (i.e., the equation of state, specific heat, surface energy) and in determining the correlation consecutively. The statistical theories of the critical point given by Mayyer (Ref. 2) and Fisher (Ref. 3) entail significant mathematical difficulties, which have not yet been surmounted, and are valid only for the case of rarefied gases. Lee and Yang (Ref. 4) constructed a theory of condensation, employing the model of Ising. Their theory is applicable to the liquid phase, but is not entirely clear in physical terms in its present form. Recently, Gersch and Berlin examined a spherical grid gas (Ref. 5).

One specific characteristic of statistical theories is the necessity of a passage to the limit, with which it is possible to determine the

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* Note: Numbers in the margin indicate pagination in the original foreign text.

decomposition of a system into two phases. The book by Khill (Ref. 6) presents a rather comprehensive analysis of the statistical theories.

In a study by the author and R. L. Stratonovich (Ref. 7), a new approach to the problem being studied was pointed out. In essence, the study (Ref. 7) presented the statistical dynamics of an equilibrium heterophase system. However, in this work we confine ourselves to examining only the general expression for the thermodynamic potential of a system and to an analysis of the equation of state. Later, in (Ref. 8) we determined the correlation of the system, and a formula was obtained for the intensity of scattered light close to the critical point. This article represents a direct continuation of the studies (Ref. 7) and (Ref. 8). We shall calculate the surface energy between phases below the critical temperature. We shall study the conduct of derivatives of the thermodynamic potential with respect to temperature and the external parameter, as a function of temperature and the external parameter. We shall provide a method for determining the critical parameters of a system.

1. As is well known, there is no clear information on the properties of a surface layer between phases in the canonical method given by Gibbs. Therefore, it is necessary to solve an independent problem in order to calculate the surface energy. Let us write an expression for the thermodynamic potential of a system (see appendix)

$$\Phi = \frac{\Phi_1 + \Phi_{-1}}{2} - \sqrt{\left(\frac{\Phi_1 - \Phi_{-1}}{2}\right)^2 + \Phi_0^2}. \qquad (1)$$

Here $\Phi_{\perp 1} = N\varphi_{\perp 1}$ are the thermodynamic phase potentials calculated on /55

the basis of Gibbs' method: $m = N \cdot m_j$ is the total number of particles in the system: $\Phi_0 = \Theta m \cdot q$; $q = \frac{e^{-\beta U}}{m_j}$, U is the potential of interaction between molecules of different phases (below, U is assumed to be a constant). Let us employ the following simple reasoning. Let us assume that there is only one phase in the system - for example, 1. There is no boundary between the phases at low temperatures. The thermodynamic potential of such a system is Φ_1. When there is a mixture of two phases, a boundary appears for $T < T_\kappa$ and $\Phi_0 < \Phi_{0,\kappa}$, when the system decomposes into phases. Consequently, the surface energy between the phases Σ equals the excess thermodynamic potential, which is caused by the appearance of a boundary:

$$\Sigma(a, \Theta) = \frac{\Phi_{-1} - \Phi_1}{2} - \sqrt{\left(\frac{\Phi_1 - \Phi_{-1}}{2}\right)^2 + \Phi_0^2}. \qquad (2)$$

In accordance with experiment, at the critical point $(\Phi_1(a_\kappa, \Theta_\kappa) = \Phi_{-1}(a_\kappa, \Theta_\kappa); \Phi_0 \ll 1)$ the surface energy becomes zero.

It is of interest to estimate the dimensions of the surface layer. For this purpose, we can utilize the smoothed correlation function (Ref. 8):

$$K(l) = \frac{1}{4} \frac{q^2}{\left[\left(\frac{\varphi_1 - \varphi_{-1}}{2}\right)^2 + q^2\right]} \exp\left\{-2m_1 \sqrt{\left(\frac{\varphi_1 - \varphi_{-1}}{2}\right)^2 + q^2} \cdot |l|\right\} \qquad (3)$$

($m_1 = \frac{m_j}{v_j}$ is the particle density).

Utilizing (3), we can find the effective thickness of the surface layer (see [Ref. 4]):

$$d(a, \Theta) \sim \frac{\text{const}}{2m_1 \sqrt{\left(\frac{\varphi_1 - \varphi_{-1}}{2}\right)^2 + q^2}}. \tag{4}$$

Close to the critical point, it is advantageous to expand the difference $\varphi_1 - \varphi_{-1}$ in series:

$$\varphi_1 - \varphi_{-1} = A(\Theta - \Theta_\kappa) + B(a - a_\kappa), \tag{5}$$

where

$$A = \left.\frac{\partial \varphi_1}{d\Theta}\right|_{\Theta=\Theta_\kappa} - \left.\frac{d\varphi_{-1}}{d\Theta}\right|_{\Theta=\Theta_\kappa}; \quad B = \left.\frac{\partial \varphi_1}{\partial a}\right|_{a=a_\kappa} - \left.\frac{\partial \varphi_{-1}}{da}\right|_{a=a_\kappa}.$$

It can be seen from (5) that the thickness of the surface layer increases according to the following law as the critical point is approached:

$$d \sim \frac{\text{const}}{|\Theta - \Theta_\kappa|}, \tag{6}$$

if it moves along the isobar, and

$$d \sim \frac{\text{const}}{|a - a_\kappa|} \tag{7}$$

for movement along the isotherm.

At the critical point the thickness of the layer has the finite value:

$$d \sim \text{const}\, q. \tag{8}$$

A change in the surface energy is described by the approximate law: /56

$$\Sigma(a, \Theta) \sim A(\Theta_\kappa - \Theta) + B(a_\kappa - a). \tag{9}$$

Let us write the expressions for surface energy and thickness of the surface layer for a real gas model. In the case of the gas (see [Ref. 7]):

$$\varphi_1 = \frac{5}{2} m_j \Theta \ln \beta p b + m_j p b ,$$

$$\varphi_{-1} = - m_j \alpha(\Theta) + m_j p b , \qquad (10)$$

$$\left(\beta = \frac{1}{\Theta} ; \quad \Theta = \kappa T\right)$$

(the mobility of gas molecules is taken into account additionally when calculating ϕ_1).

Substituting (10) in (2) and (4), we obtain (Figure 1):

$$\Sigma = - \frac{\ln x}{2} - \sqrt{\left(\frac{\ln x}{2}\right)^2 + q^2} \qquad (11)$$

and

$$d \sim \frac{\text{const}}{2 m_1 \sqrt{\left(\frac{\ln x}{2}\right)^2 + q^2}} \qquad (12)$$

$$x \sim \frac{1}{\Theta} \qquad \left(x = (\beta p b)^{\frac{5}{2}} \cdot e^{\beta \alpha}\right) .$$

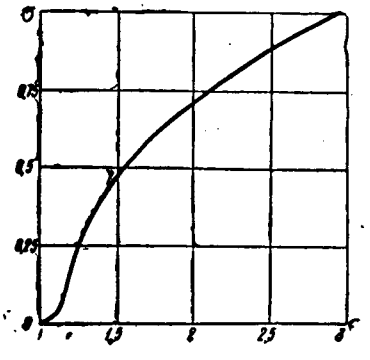

Figure 1

Dependence of Surface Energy Σ on Temperature

2. Let us now study the derivatives of the thermodynamic potential. Differentiating (1) with respect to temperature, we can determine the entropy and specific heat of the system:

$$S(a,\Theta)=\frac{S_1+S_{-1}}{2}-\frac{1}{4}\frac{(\Phi_1-\Phi_{-1})(S_1-S_{-1})-4\kappa\Phi_0\frac{d\Phi_0}{d\Theta}}{\sqrt{\frac{(\Phi_1-\Phi_{-1})^2}{2}+\Phi_0^2}}, \tag{13}$$

$$C_a(a,\Theta)=\frac{C_1+C_{-1}}{2}-\frac{1}{4}\times$$

$$\times\frac{(C_1-C_{-1})(\Phi_1-\Phi_{-1})-\kappa\Theta\left(\frac{\partial\Phi_1}{\partial\Theta}-\frac{\partial\Phi_{-1}}{\partial\Theta}\right)^2-4\kappa\Theta\left(\frac{\partial\Phi_0}{\partial\Theta}\right)^2-4\kappa\Theta\Phi_0\frac{\partial^2\Phi_0}{\partial\Theta^2}}{\sqrt{\left(\frac{\Phi_1-\Phi_{-1}}{2}\right)^2+\Phi_0^2}}-$$

$$-\frac{\kappa\Theta}{16}\frac{\left[(\Phi_1-\Phi_{-1})\left(\frac{\partial\Phi_1}{\partial\Theta}-\frac{\partial\Phi_{-1}}{\partial\Theta}\right)-4\Phi_0\frac{\partial\Phi_0}{\partial\Theta}\right]^2}{\left[\left(\frac{\Phi_1-\Phi_{-1}}{2}\right)^2+\Phi_0^2\right]^{3/2}}. \tag{14}$$

It is possible to find the corresponding derivatives with respect /57 to the external parameter. For the second derative, which determines the inclination of the equation of state curve, we have:

$$\frac{\partial^2\Phi}{\partial a^2}=\frac{\frac{\partial A_1}{\partial a}-\frac{\partial A_{-1}}{\partial a}}{2}-\frac{1}{4}\frac{(A_1-A_{-1})^2+\left(\frac{\partial A_1}{\partial a}-\frac{\partial A_{-1}}{\partial a}\right)(\Phi_1-\Phi_{-1})}{\sqrt{\left(\frac{\Phi_1-\Phi_{-1}}{2}\right)^2+\Phi_0^2}}+$$

$$+\frac{1}{16}\frac{[(\Phi_1-\Phi_{-1})(A_1-A_{-1})]^2}{\left[\left(\frac{\Phi_1-\Phi_{-1}}{2}\right)^2+\Phi_0^2\right]^{3/2}}. \tag{15}$$

When the interaction between phase molecules can be disregarded

(i.e., $|\Phi_1 - \Phi_{-1}| \gg 2\Phi_0$), expressions (13), (14), and (15) change into relationships of the following type:

$$C_a(a, \theta) = \frac{C_1 + C_{-1}}{2} - \frac{C_1 - C_{-1}}{2} \operatorname{sgn}(\Phi_1 - \Phi_{-1}). \qquad (16)$$

Let us examine, for example, the conduct of specific heat close to the critical point. The following term plays the basic role in this region:

$$C_a(a, \theta) \sim \frac{\kappa\theta}{4} \frac{\left(\frac{\partial\Phi_1}{\partial\theta} - \frac{\partial\Phi_{-1}}{\partial\theta}\right)^2}{\sqrt{\left(\frac{\Phi_1 - \Phi_{-1}}{2}\right)^2 + \Phi_0^2}}. \qquad (17)$$

This leads to the fact (5) that the specific heat changes according to the following law as the critical point is approached:

$$C(a, \theta) \sim \frac{\text{const}}{|\theta - \theta_\kappa|} \qquad (18)$$

for constant $a = a_k$, or

$$C(a, \theta) \sim \frac{\text{const}}{|a - a_\kappa|} \qquad (19)$$

for constant temperature $\theta = \theta_\kappa$.

And now the conclusions can be drawn regarding $\frac{\partial^2\Phi}{\partial a^2}$ and the subsequent derivatives.

Thus, at the critical point the derivatives of the thermodynamic potential are continuous functions of temperature and pressure. At the same time, we should point out the slow change in the first derivatives (see graphs for the equation of state [Ref. 7]) and the sharp increase in the second derivatives (18), (19) in this interval of temperature and pressure.

Let us give a formula for specific heat of a real gas at constant pressure (Figure 2):

$$C_p(p,\Theta)=\frac{\frac{5}{2}R+C_{ж}}{2}-\frac{1}{4}\frac{\left(\frac{5}{2}R-C_{ж}\right)\ln x-\frac{25}{4}R\Delta^2}{\sqrt{\left(\frac{\ln x}{2}\right)^2+q^2}}-$$

$$-\frac{25}{64}R\frac{(\ln x\cdot\Delta)^2}{\left[\left(\frac{\ln x}{2}\right)^2+q^2\right]^{3/2}}, \qquad (20)$$

$$\left(\Delta=\frac{\partial\alpha}{\partial\Theta}-1-\frac{2}{5}\beta\alpha\right).$$

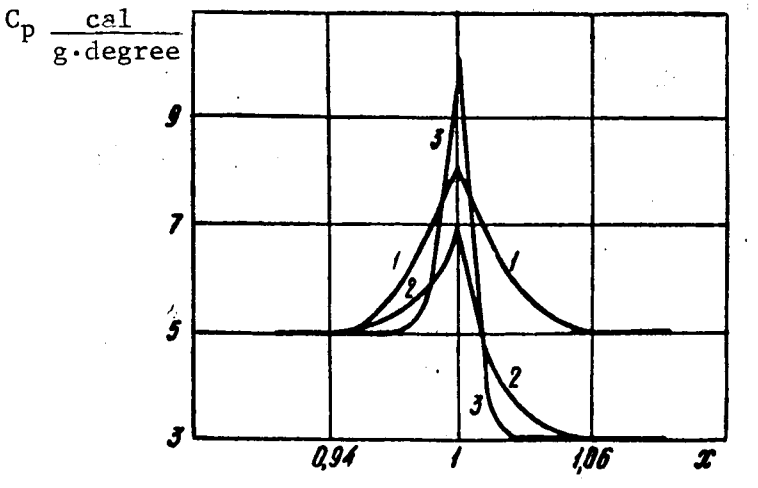

Figure 2

Dependence of Specific Heat on Pressure at Different Temperatures $\Delta=10^{-1}$. 1-$C_{ж}$ = 5cal/g·degree, $q=10^{-2}$ 2-$C_{ж}$ = 3cal/g·degree, $q=10^{-2}$; 3-$C_{ж}$ = 3cal/g·degree, $q = 5\cdot10^{-3}$.

The terms containing q and its derivatives are small for a real gas, and we can omit them.

Close to the critical point, from the equation of state (see [Ref. 7])

$$V = bm + \frac{\Theta m}{2p}\left(1 - \frac{1}{2}\frac{\ln\beta pb + \beta\alpha}{\sqrt{\left(\frac{\ln\beta pb + \beta\alpha}{2}\right)^2 + q^2}}\right) \qquad (21)$$

we can readily determine the dependence of phase volumes on temperature and pressure

$$V = V_\kappa \pm q\,[\Lambda\,|\,\Theta - \Theta_\kappa\,| + \mathrm{B}\,(p - p_\kappa)]. \qquad (22)$$

The sign + pertains to gas; the sign - pertains to liquid. We can readily find the following expression for heat conversion from (13):

$$Q = \Theta\,[\mathrm{A}\,|\Theta - \Theta_\kappa| + \mathrm{B}\,|p - p_\kappa|]. \qquad (23)$$

For $\Theta = \Theta_\kappa$ and $p = p_\kappa$, (22) and (23) become invalid - just as do (18) and (19) - and it is necessary to employ accurate formulas.

3. In the preceding reports (Ref. 7, 8), we did not formulate with sufficient clarity the method for determining the critical parameters of a system. Let us now turn to this in greater detail. The equation of thermodynamic potentials $\Phi_1(a, \Theta) = \Phi_{-1}(a, \Theta)$ determines the curve for /59 phase equilibrium a = f(θ). This curve terminates at the point which is called the critical point. Because it is impossible to determine the critical point from the condition of phase equilibrium, a series of additional conditions are introduced in thermodynamics in order to determine it: $\frac{\partial p}{\partial v} = 0$, stability $\frac{\partial^2 p}{\partial^2 v^2} = 0$, $\frac{\partial^3 p}{\partial v^3} < 0$. The surface phenomena are usually examined separately, and are not included in a determination of the critical parameters.

In the theory developed, the disappearance of the surface energy

$$\Sigma(a_\kappa, \Theta_\kappa) = 0 \tag{24}$$

gives the first condition, which connects the critical parameters of the system.

In addition, just as was done in (Ref. 4), it is possible to show [see (3)] that the state of the system at the critical point would be absolutely unstable, if q = 0.

$$d \to \infty; \quad \left(\frac{\partial^2 \Phi}{\partial p^2}\right)_{T_\kappa} \to \infty.$$

The latter conditions should coincide with the normal thermodynamic criterion for stability loss at the critical point. In view of the fact that $q(\Theta_\kappa) \neq 0$, for the case examined above, the critical point is stable.

In the region of biphase states ($T < T_k$, $q \ll 1$), the system is almost unstable. Above the critical temperature ($q \sim 1$), and also in a definite pressure region below the critical temperature, the system is stable. Even in the case of a very simple model (U const), it is possible to determine the following from an experiment for the maximum of specific heat and intensity of scattered light:

$$q(\Theta_\kappa) = \delta \tag{25}$$

and to find the critical temperature.

Substituting it in (24), we find the critical pressure, and then the critical volume from the equation of state. In the general case, the second condition connecting the critical parameters has the following form:

$$q(\Theta_\kappa, p_\kappa) = \delta. \tag{26}$$

Unfortunately, the explicit dependence of the thermodynamic potential of a liquid $\alpha(\theta)$ on temperature is still not known, and therefore we cannot calculate the critical parameters for a real gas model.

Conclusions

A statistical theory for the critical point is presented. We obtained smoothed dependences, instead of the curves which are characteristic for thermodynamics and which consist of three parts: liquid, region of condensation, and gas. The continuity of the changes from one part to another is a principal feature, and is due to the correct calculation of the statistical factors. The dependences which are found can be interpreted experimentally as jumps in a narrow interval of temperature and pressure. The theory can be applied to an examination of phase changes in other systems.

Appendix /60

We would like to present a brief summary of the expressions for the thermodynamic potential of an equilibrium biphase system. Our basic assumption contains the postulate that the thermodynamic potential of the biphase system equals:

$$\Phi(p, \theta) = -\Theta \ln \lambda_1, \tag{27}$$

where λ_1 is the largest eigen value of the matrix.

$$\hat{C} = \begin{pmatrix} Z_1 Z_0 \\ Z_0 Z_{-1} \end{pmatrix}, \tag{28}$$

while

$$Z_s = \frac{1}{h^{3m_s} m_s!} \int \cdots \int \exp\left\{-\left[\beta \sum_{1<i<j<m_s} \frac{p_i^2}{2m} + U(|q_{s,i} - q_{s,j}|) + pV_s\right]\right\} dq_{s,i} \ldots dq_{s,j} dV_s,$$

$$(m_s = \pm 1), \tag{29}$$

$$Z_0 = \frac{1}{h^{3\left(\frac{m_1+m_2}{2}\right)} \left(\frac{m_1+m_2}{2}\right)!} \int \cdots \int \exp\left\{-\left[\beta \sum_{\substack{1<i<m_1 \\ 1<j<m-1}} U(|q_{1,i} - q_{-1,j}|) + \right.\right.$$

$$\left.\left. + p(V_1 + V_{-1})\right]\right\} \times dq_{1,i} \ldots dq_{-1,j} dV_1 dV_{-1},$$

q1,i(i=1,2...m_1) lies at V_1,

q-1,j(j=1,2...m_{-1}) lies at V_{-1}.

The first two terms in (29) represent the statistical sums of the system phases and the latter term represents the interaction between phases. Because

$$Z_s = e^{-\beta \Phi_s(p,\vartheta)}, \tag{30}$$

then expanding the exponent in series in (30), λ_1 can be represented in the form:

$$\lambda_1 = 1 + \lambda_0, \tag{31}$$

where

$$\lambda_0 = -\frac{\Phi_1 + \Phi_{-1}}{2} + \sqrt{\left(\frac{\Phi_1 - \Phi_{-1}}{2}\right)^2 + \Phi_0^2}. \tag{32}$$

Substituting (31) in (27), we obtain (1). For a more detailed treatment of this subject, consult (Ref. 7).

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